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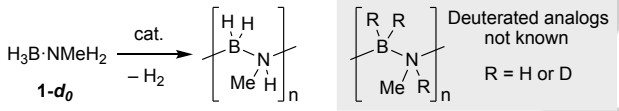
A General, Rhodium-Catalyzed, Synthesis of Deuterated Boranes and *N*–Methyl Polyaminoboranes

Annie L. Colebatch,[a] Benjamin W. Hawkey Gilder,[a] George R. Whittell,[b] Nicola L. Oldroyd,[b] Ian Manners[b] and Andrew S. Weller*[a]

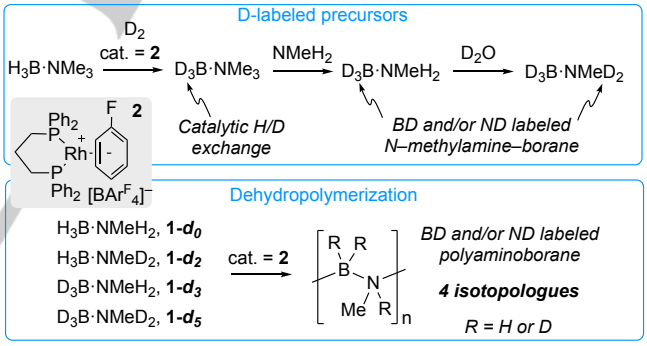
Abstract: The rhodium complex [Rh(Ph$_2$PCH$_2$CH$_2$CH$_2$PPh$_2$)(η^6–FC$_6$H$_5$)][BAr$^F_4$], **2**, catalyzes BH/BD exchange between D$_2$ and the boranes H$_3$B·NMe$_3$, H$_3$B·SMe$_2$ and HBpin, facilitating the expedient isolation of a variety of deuterated analogues in high isotopic purities, and in particular the isotopologues of *N*-methyamineborane: R$_3$B·NMeR$_2$ **1-*d*$_x$** (R = H, D; x = 0, 2, 3 or 5). It also acts to catalyze the dehydropolymerization of **1-*d*$_x$** to give deuterated polyaminoboranes. Mechanistic studies suggest a metal-based polymerization involving an unusual hybrid coordination insertion chain-growth/step-growth mechanism.

Deuterated polymeric materials can possess different properties to their hydrogen-isotopologues, and their synthesis and characterization is thus of considerable interest.[1] The tailoring of chemical, physical and material characteristics of polymers by deuteration has been exploited in a variety of areas, such as the modification of optoelectronic[2] and electromagnetic[3] properties, structure,[2, 4] analysis of polymer chain dynamics and morphology using small angle neutron scattering,[5] spectroscopic studies,[4a, 6] and nuclear applications.[7]



Scheme 1. Dehydropolymerization of H$_3$B·NMeH$_2$.

One area which is the subject of current attention in main group polymer chemistry is the dehydropolymerization of *N*–methylamineborane, H$_3$B·NMeH$_2$ **1-*d*$_0$**, for the preparation of BN chain polyaminoboranes (H$_2$BNMeH)$_n$,[8] that are isoelectronic to polypropylene. Although a range of transition metal catalysts are known to catalyze dehydropolymerization, Scheme 1,[9] the preparation of deuterated analogues, e.g. (R$_2$BNMeR)$_n$, R = H or D, has not been reported. In order to prepare such *d*-labeled *N*–methylpolyaminoboranes cost-effective access to gram–scale quantities of the amine–borane isotopologues H$_3$B·NMeD$_2$ (**1-*d*$_2$**), D$_3$B·NMeH$_2$ (**1-*d*$_3$**) and D$_3$B·NMeD$_2$ (**1-*d*$_5$**) in high isotopic purity is required. The limited commercial availability,[10] expense and restricted storage lifetime[11] of the precursor D$_3$B·THF[12] necessitated exploration of an alternative route to **1-*d*$_x$** (x = 3, 5), namely *catalytic* BH/BD exchange at preformed amine–boranes using D$_{2(g)}$.[13] In this contribution we report that [Rh(dppp)(η^6–FC$_6$H$_5$)][BAr$^F_4$] (**2**, dppp = bis(diphenylphosphino)propane, Ar^F = 3,5–(CF$_3$)$_2$C$_6$H$_3$),[14] acts as a simple and practical precatalyst for BH/BD exchange at H$_3$B·NMe$_3$, facilitating reliable access to the four isotopologues of R$_3$B·NMeR$_2$ (R = H, D) in good isolated yield and high isotopic purity (Scheme 2). The scope of this H/D exchange strategy is further demonstrated by extension to the synthesis of d-labeled boronic esters. Subsequent dehydropolymerization of R$_3$B·NMeR$_2$, also using **2**, provides the variously isotopically-enriched polyaminoboranes (R$_2$BNMeR)$_n$. Mechanistic studies suggest dehydropolymerization occurs via a sequential coordination insertion chain-growth/step-growth mechanism.



Scheme 2. H/D exchange and dehydropolymerization.

As discussed, the preparation of deuterated polyaminoboranes requires the synthesis of appropriate d-labeled precursors. Although BH/BD exchange has been observed in transition metal borane σ-complexes,[15] examples of catalytic H/D exchange for the synthesis of deuterated boranes are scarce. Examples include reaction of pinacol- or catecholborane with D$_2$ using [Ru(PCy$_3$)$_2$H$_2$(H$_2$)$_2$][16] or [IrHCl{C(N^{t}BuCH)$_2$}{C(N^{t}BuCH)-(CN(CCH$_2$Me$_2$)CH)$_2$}][17] catalysts; although the latter complex was also shown to be ineffective for deuteration of H$_3$B·L (L = SMe$_2$, RN(CH$_2$CH$_2$)$_2$O, R = H, Me). H/D exchange of H$_3$B·NMe$_3$ has been reported using a RuHCl(PPh$_3$)$_3$ catalyst, by bubbling D$_2$ through a toluene solution at 100°C for 24 hours,[18] but no comment as to the yield obtained was made.

Complex **2** has been shown to promote B–H activation of primary and secondary amine–boranes.[14] This proceeds via initial oxidative cleavage of a Rh···H–B sigma interaction to give a base-stabilized boryl hydride, as indicated by complimentary studies using phosphine boranes.[19] Such an intermediate could

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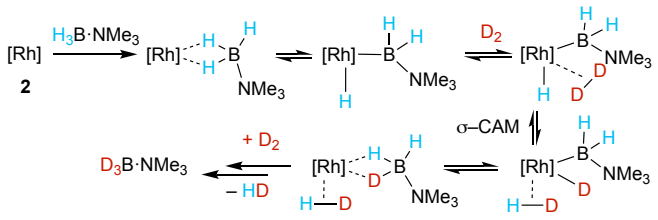
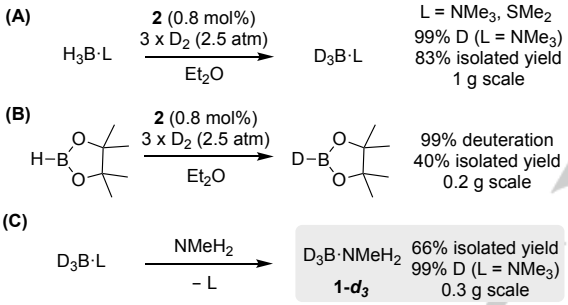
also be captured by exogenous D_2 leading to H/D exchange,[15e] via σ-complex assisted metathesis (σ–CAM),[20] Scheme 3.



Scheme 3. Proposed mechanism for H/D exchange.

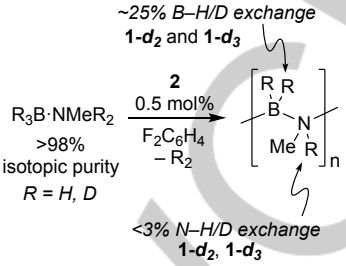
$H_3B{\cdot}NMe_3$ is an ideal substrate for such BH/BD exchange as it can be sublimed, is air-stable, does not have N−H groups needed for onward dehydrogenation, and also forms a σ−complex with **2**, a precursor to B−H activation.[14a] Existing methods for the formation of $D_3B{\cdot}NMe_3$ include acid- or ruthenium-catalyzed H/D exchange of $H_3B{\cdot}NMe_3$ using D_2O (which suffers from competitive hydrolysis),[21] ion exchange,[22] or crown-ether-catalyzed reaction of $NaBD_4$ with NMe_3HCl.[23]



Scheme 4. (A) Deuteration of $H_3B{\cdot}L$ (L = NMe_3, SMe_2) catalyzed by **2**. D_2 added in 3 x 3-fold excess. **(B)** Deuteration of HBpin. Conditions as for **(A)**. **(C)** Preparation of $D_3B{\cdot}NMeH_2$ (**1-*d*$_3$**; L = NMe_3, SMe_2).

Initial screening showed that **2** promotes BH/BD exchange in $H_3B{\cdot}NMe_3$ with D_2 in Et_2O, THF or 1,2−$F_2C_6H_4$ solvents. Limited reactivity was observed in CH_2Cl_2. Low boiling Et_2O was selected for further studies, which can be removed under a gentle vacuum whilst minimizing loss of $D_3B{\cdot}NMe_3$. Optimized catalytic H/D exchange using **2** (0.8 mol%, Et_2O, 2.5–12 hrs, Table S1) gave $D_3B{\cdot}NMe_3$ in isolated yields of up to 83% and up to 99% isotopic purity (~ 1 gram scale), Scheme 4A. Monitoring the rate of deuteration by in situ NMR spectroscopy showed that the reaction proceeded only upon agitation of the solution, indicating the rate is controlled by diffusion between the gas and liquid phases. Rapid stirring and sufficient reaction times were thus used in the bulk synthesis. Catalyst **2** is required, as there is no reaction observed in its absence.

Applying these conditions to the borane reagents $H_3B{\cdot}SMe_2$ and HBpin produced $D_3B{\cdot}SMe_2$ and DBpin, demonstrating the broader applicability of the method, Scheme 4B. DBpin (99% D) was produced in 95% spectroscopic yield and isolated in 40% yield after distillation. For $D_3B{\cdot}SMe_2$, H/D exchange proceeds more slowly (days), and vacuum distillation to remove the catalyst provides an Et_2O solution of $D_3B{\cdot}SMe_2$ (88% D) that can be used directly in onward reactions. Both $D_3B{\cdot}SMe_2$ and $D_3B{\cdot}NMe_3$ act as precursors to $D_3B{\cdot}NMeH_2$, **1-*d*$_3$**, by reaction with $NMeH_2$, with full retention of isotopic purity, Scheme 4C. **1-*d*$_5$** can in turn be prepared by treatment of **1-*d*$_3$** with D_2O (Supporting Materials). **1-*d*$_2$** can similarly be prepared from **1-*d*$_0$**,[12] thus providing access to the four isotopologues arising from H/D exchange at B or N in high isotopic purities.



Substrate	M_n g mol^{-1}	Đ
$H_3B{\cdot}NMeH_2$, **1-*d*$_0$**	27,700	1.84
$H_3B{\cdot}NMeD_2$, **1-*d*$_2$**	31,100	1.63
$D_3B{\cdot}NMeH_2$, **1-*d*$_3$**	20,700	1.96
$D_3B{\cdot}NMeD_2$, **1-*d*$_5$**	32,700	1.84

Scheme 5 Dehydropolymerization of $R_3B{\cdot}NMeR_2$ (R = H, D). Conditions: 0.4 M [$R_3B{\cdot}NMeR_2$] (R = H, D), 90 minutes, system open to Ar flow.

With these four isotopologues of **1-*d*$_x$** in hand, the dehydropolymerization catalyzed by **2** was studied, Scheme 5. All four precursors produced off-white polymeric material using 0.5 mol% **2** (0.4 M [**1-*d*$_x$**], 1,2−$F_2C_6H_4$, 90 min) in moderate isolated yield (up to 67%). ^1H and ^2H NMR spectroscopy of the polymer produced using **1-*d*$_2$** and **1-*d*$_3$** revealed the presence of both B−H and B−D environments. This indicates that BH/BD scrambling occurs during the reaction (~ 25%), likely due to reversible H/D exchange at a boryl hydride intermediate with liberated HD (e.g. Scheme 3).[15a] Very little NH/ND scrambling was observed (less than 3%), consistent with N−H activation being irreversible.[24] The ^{11}B NMR spectra of isolated polymer produced using **1-*d*$_x$** were very similar to those reported previously, showing a broad resonance at ca. δ –6 (Figure S4). A small shoulder to lower field of the main chain 'BH_2' signal, which has been attributed to BN_3H or BN_4 units,[9l,25] was also observed in all samples (δ +2).

Gel permeation chromatography (GPC), from which polymer molecular weight was determined from relative hydrodynamic radii using a refractive index (RI) detector, showed a modest variation in molecular weight (ca. 10,000 g mol^{-1}) with isotope distribution. No strong trend is evident, although **1-*d*$_3$** produced the smallest polymer. Whether this data is indicative of any changes in chain length, which would result from perturbation of the reaction kinetics upon deuteration (e.g. rate of propagation versus rate of termination), is not clear. Non-covalent interactions, such as N–H···H–B dihydrogen bonding, are likely to play a pivotal role controlling the polymer conformation in polyaminoboranes,[26] and the magnitude of such interactions will be affected by isotopic substitution. Such effects on polymer conformation have been noted in polystyrene, wherein a 0.5% increase in volume was observed upon substitution of H for D.[4b] These polymers were also studied by electrospray ionization mass spectrometry (ESI–MS, positive mode, CH_2Cl_2 solvent, Figures 1 and S5 – S6). The maximum observed *m/z* is ca. 3,000 for all samples, indicating a degree of polymerization (DP) ~ 70 as measured by this technique. This is much lower than the

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molecular weights determined by GPC (e.g. DP = 690 for **1-*d*$_5$**), but replicates the maximum *m/z* measured by ESI-MS for high molecular weight ($H_2BNMeH)_n$ (M_n = 107,000 g mol^{-1}), demonstrating the limitation of ESI–MS for molecular weight determination in polyaminoboranes, as noted previously.[9b]

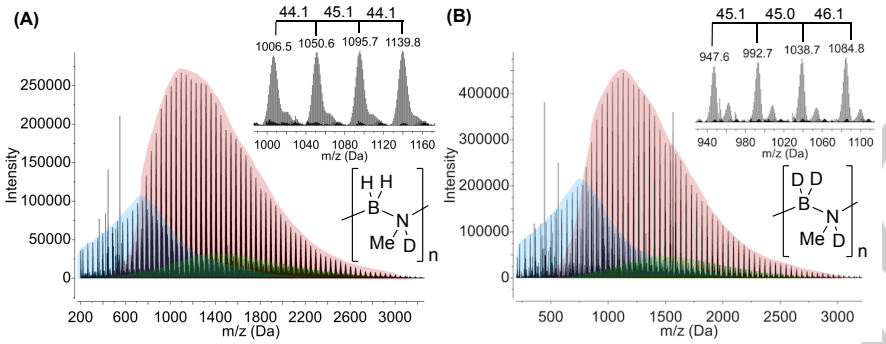


Figure 1. ESI-MS of polyaminoborane from the dehydropolymerization of $H_3B{\cdot}NMeD_2$ (**1-*d*$_2$**) and $D_3B{\cdot}NMeD_2$ **(1-*d*$_5$)** showing the three distributions present: $[(R_2BNMeR)_nR]^+$ (blue), $[R_2MeN(R_2BNMeR)_nR]^+$ (red) and $[R(R_2BNMeR)_nBR_2]^+$ (green); R = H or D.

Nevertheless, with this caveat, useful information regarding repeat units can be obtained. The ESI-MS for **1-*d*$_0$** shows a major distribution corresponding to $[H_2MeN(H_2BNMeH)_nH]^+$, alongside two minor distributions which best match $[(H_2BNMeH)_nH]^+$ and $[(H_2BNMeH)_nBH_2]^+$ (Figure S5).[9b, 27] All three distributions have repeat units of *m/z* = 43.1 ($H_2B{=}NMeH$). Polymer prepared from **1-*d*$_2$** (Figure 1A) and **1-*d*$_3$** (Figure S6) showed similar isotope patterns suggesting monomer repeat units of both *m/z* = 44.1 ($BNMeH_2D$) and 45.1 ($BNMeHD_2$), consistent with the NMR spectroscopic data. Interestingly, H/D scrambling was also observed for polymer prepared from **1-*d*$_5$** (Figure 1B) with an isotopic distribution that best fits monomer repeat units ($BNMeD_3$):($BNMeD_2H$) in a 4:1 ratio (m/z = 46.1, 45.1). This is despite ^{1}H NMR spectroscopy indicating levels of B−H and N−H incorporation less than 3%, that reflects the isotopic purity of precursor **1-*d*$_5$**, and suggests that H/D exchange can occur under ESI-MS analysis, likely from adventitious water in the solvent.

Thermogravimetric analysis (TGA, 10°C/min, 25 – 500°C) demonstrated a slight variation in decomposition temperature (T_d) across the range of polymer isotopologues (125 – 139°C), that suggests a correlation with the site of deuteration, with BD substitution promoting slightly lower T_d, although the differences are small (Table S4). Interestingly, polymers with ND groups give lower ceramic yields: 36%, **1-*d*$_0$**; 10%, **1-*d*$_2$**; 46%, **1-*d*$_3$**; 20% **1-*d*$_5$**. Previously reported high molecular weight $(H_2BNMeH)_n$ (M_n = 107,000 g mol^{-1}) gave TGA data (T_d = 150°C, ceramic yield 25%)[9b] that is different from medium molecular weight material from **1-*d*$_0$** (134ºC, 36%) suggesting that polymer chain length and/or any entrained[25b, 28] catalyst also affect thermal decomposition processes. These data on polyaminoborane samples of similar molecular weight prepared from the same catalyst suggest isotopic substitution has a measurable effect on thermal decomposition characteristics, with the lowest T_d and ceramic yield provided by BD and ND substitution respectively.

Little mechanistic detail for amine–borane dehydropolymerization catalyzed by **2** is known beyond observation of an induction period and $[Rh_2(\mu{-}H)(\mu{-}H_2BNMeH)(dppp)_2][BAr^F{}_4]$ as the first formed species.[14] The closely related precatalyst $[Rh(\eta^2{-}H_2BN{-}Me_3CH_2CH_2{}^tBu)(Xantphos)][BAr^F{}_4]$ has been studied in more detail, and mechanistic studies suggest a single–site coordination / dehydrogenation / insertion chain-growth mechanism for dehydropolymerization.[9k] This is signaled by an inverse relationship between M_n and catalyst loading, H_2 acting as a termination agent to strongly modify chain length, and H_2 release studies (0.2 M **1-*d*$_x$**) that show an induction period followed by a temporal profile that is best modelled using saturation kinetics (i.e. quasi irreversible substrate binding). Although similar kinetic profiles for H_2 release are observed using **2** and all the isotopologues of **1-*d*$_x$** (Figure S8), initially suggesting a similar mechanism (*vide infra*), significant variability in rate between different batches of amine–borane and solvent was noted, and thus we are reluctant to interpret the effect of isotopic substitution on any turnover limiting step. There was no significant variability in the final molecular weight of polymer isolated between different batches. We have recently made similar observations for P–alkyl substituted {Rh(Xantphos)} catalysts.[9l]

Polymer growth kinetics thus focused on **1-*d*$_0$** using the same batch of substrate and solvent. At the limit these can be chain-growth, characterized by significant polymerization and unreacted monomer being observed at early reaction times; or step-growth, where complete monomer consumption (to form dimers and oligomers) is achieved early and high molecular weights are only reached at very high conversions.[29] A plot of conversion of **1-*d*$_0$** versus M_n (Figure 2) reveals an unusual profile, that captures elements of *both* chain- and step-growth.

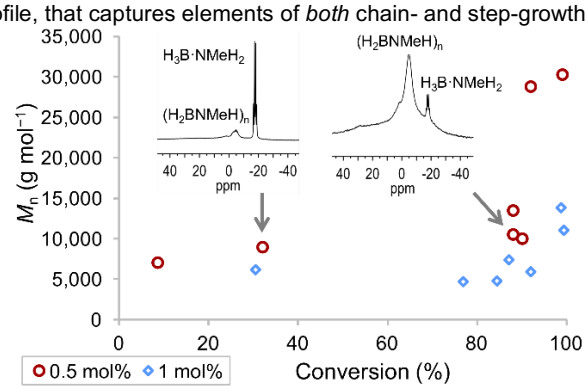
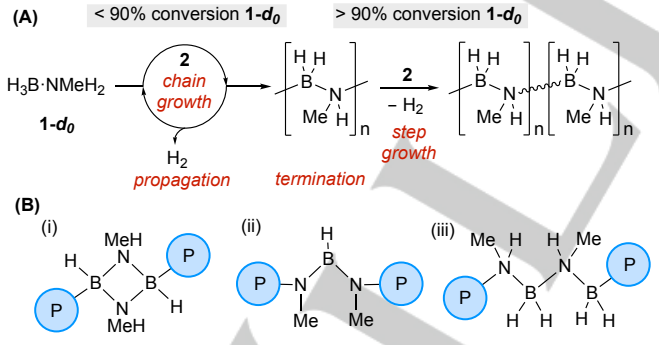


Figure 2. Molecular weight of $(H_2BNMeH)_n$ versus conversion of **1-*d*$_0$** for dehydropolymerization catalyzed by **2** at 1 mol % (◊) or 0.5 mol% (○) (0.4 M [**1-*d*$_0$**]). Inset: ^{11}B NMR spectra at low (left) and high (right) conversion. Each data point comes from polymer isolated from a single experiment quenched after the appropriate time using excess PPh_3.

These experiments show that at 0.5 mol% loadings of **1** between low (<10%) to high (~90%) conversions, medium molecular weight polyaminoborane was observed (M_n ~ 10,000 g mol^{-1}) alongside significant, but diminishing, quantities of unreacted **1-*d*$_0$**, consistent with a *chain-growth* process. However, at very high conversions (>90%) a dramatic increase in molecular weight was observed to M_n ~ 30,000 g mol^{-1}, characteristic of a *step-growth* polymerization. An alternative explanation is that late–stage chain branching leads to a dramatic increase in hydrodynamic radius at high conversion. However as the ^{11}B NMR spectrum of isolated polymer at 99% conversion closely resembles those for the materials isolated at lower conversions, we discount this particular process (Figure S7).

We thus propose a hybrid mechanism for dehydropolymerization, in which chain-growth polymerization occurs at initially high concentrations of **1-*d*$_0$**; but at high conversions, i.e. low [**1-*d*$_0$**], an alternative step-growth coupling becomes dominant. Support for the early–stage mechanism being single–site coordination / dehydrogenation / insertion chain–growth comes from the inverse dependence of M_n upon catalyst loading during the chain–growth phase, that is amplified by the late–stage step–growth process: 0.25 mol%, M_n = 43,300 g mol^{-1}; 0.5 mol%, M_n = 27,700 g mol^{-1}; 1 mol%, M_n = 10,100 g mol^{-1} (Table S2).[30] H_2 also acts as a chain transfer agent as shown by significantly lower degrees of polymerization in a closed system (0.5 mol% **2**, M_n = 4,700 g mol^{-1}, *Đ* 2.04) when H_2 is allowed to build up. Support for the late–stage step-growth coupling comes from treatment of lower molecular weight $(H_2BNMeH)_n$ (M_n = 6,900 g mol^{-1}, *Đ* 2.25) with 0.5 mol% **2** for 90 minutes, that provides an effective doubling in molecular weight (M_n = 15,000 g mol^{-1}, *Đ* 2.01), an observation which also argues against significant depolymerization occurring. In the absence of **2**, the polymer remains essentially unchanged under these conditions (M_n = 7,400 g mol^{-1}, *Đ* 2.03).



Scheme 6. (A) Proposed mechanism for overall dehydropolymerization of **1-*d*$_0$** catalyzed by **2**. **(B)** Possible step–growth coupling motifs (Ⓟ = polymer).

Based on the collected data presented a mechanistic outline for dehydropolymerization is postulated in Scheme 6A. Precatalyst **2** reacts with **1-*d*$_0$** to form an active, as yet undefined, catalyst. This active catalyst binds **1-*d*$_0$** which undergoes dehydrogenation via BH and NH activation to form a latent source of aminoborane H_2B=NMeH, which inserts into the growing polymer chain and propagation ensues. Once **1-*d*$_0$** is consumed **2** catalyzes step-growth-like coupling between the thus formed polymer chains, to ultimately deliver higher molecular weight $(H_2BNMeH)_n$. Chain-growth and subsequent step-growth is rare in polymerization chemistry, but has been observed in the copolymerization of ε-caprolactone and tetrahydrofuran using a $Lu(OTf)_3$/propylene oxide catalytic system.[31] A number of cases where simultaneous chain- and step-growth polymerization occur are known.[32]

Possible mechanisms for this step–growth process are (Scheme 6B): (i) dehydrogenation of a polymer–(BH_2NMeH_2) end group, catalyzed by **2**, to form an amino–borane end group that undergoes dimerization to form a cyclic diborazane,[33] (ii) dehydrogenative B–N coupling between amino–borane and amine–polymer end groups to give a dialkylaminoborane, polymer–NMe–BH–NMe–polymer linking unit,[34] or (iii) head to tail[9l, 35] coupling of appropriate amino–boranes. We see no evidence for a dialkylaminoborane [^{11}B ca. δ +30]; while a broad signal at ~^{11}B ca. δ +2 may be indicative of (i), that also appears broader in the deuterated samples suggesting a B–H (or B–D) group, but we cannot discount this is due to chain–branching. Importantly, this resonance is present from early stages of the reaction (evident at 9% conversion, Figure S7), and hence does not result exclusively from late-stage coupling. As ESI–MS also gives no evidence for (i) and (ii) in terms of absolute m/z, the data tentatively point towards (iii) as a probable linking motif.

In summary, **2** acts as a reliable precatalyst for H/D exchange of boranes and boronic esters to produce B−D labeled boranes in high isotopic purities using low catalyst loadings. Deuterated polyaminoboranes have been produced using the thus prepared isotopologues of $H_3B{\cdot}NMeH_2$ and found to possess physical properties largely similar to $(H_2BNMeH)_n$, with only relatively small variations in chain length and thermal decomposition characteristics. An unusual hybrid chain-growth/step-growth mechanism is proposed, with chain-growth polymerization at high [**1-*d*$_0$**], likely via a coordination-insertion mechanism, and step-growth coupling following at low [**1-*d*$_0$**]. The ability to access step-growth pathways[36] in amine−borane dehydropolymerization offers a potential route to further precisely control the molecular weight of BN–backbone polymeric materials, which will benefit from ongoing optimizations of catalyst structure, loadings and experimental conditions.

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Keywords: rhodium • deuterium • borane • dehydropolymerization • H/D exchange

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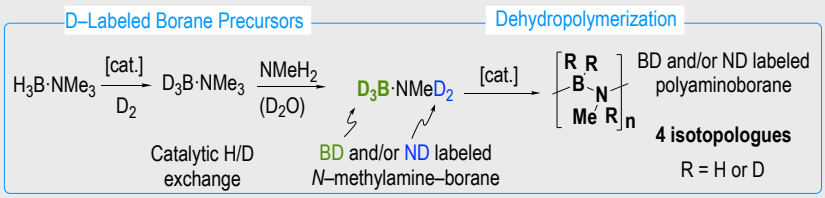

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A General, Rhodium-Catalyzed, Synthesis of Deuterated Boranes and *N*–Methyl Polyaminoboranes

Deuterated amine–boranes, prepared in high isotopic purities and yields, can be dehydropolymerized to give deuterated polyaminoboranes; for which mechanistic studies suggest an unusual hybrid coordination insertion chain-growth/step-growth mechanism.